

Union of Soviet
Socialist Republics

State Committee of
the USSR for
Inventions and
Discoveries

**DESCRIPTION OF AN INVENTION
for a Certificate of Authorship**

(11) 981217

(61) Addition to Certificate of Authorship —

(22) Filed on 7/23/80 (21) 2970691/23-26

joining with application No. —

(23) Priority —

Published 12/15/82, Byulleten' No. 46

Date specification was published 12/15/82

(51) Int. Cl.³

C 01 B 33/24

C 01 B 33/32

(53) UDC 546.284

(088.8)

(72) Authors of
the invention:

M. A. Safaryan, M. S. Manucharyan, and A. M. Safaryan

(71) Applicant:

Institute of General and Inorganic Chemistry,
Armenian Academy of Sciences

(54) METHOD FOR PREPARING A SILICATE-CALCIUM PRODUCT

The invention relates to the construction materials industry, specifically to the production of silicate materials, and can be used in the production of colorless glass for making glass stock

A method is known for preparing $\text{Na}_2\text{O} \cdot \text{CaO} \cdot 6\text{SiO}_2$ by the autoclave treatment of a mixture of sodium metasilicate, silica, and calcium metasilicate; the precipitate obtained after filtration of the autoclave slurry, containing $\text{Na}_2\text{O} \cdot \text{CaO} \cdot 6\text{SiO}_2$, is dried [1].

Drawbacks of this method are the complexity of the process for preparing sodium-calcium silicate: these are related to the necessity of first preparing sodium metasilicate and calcium metasilicate, the use of freshly precipitated starting components, which are difficult to process, the high thermal power consumption, the complexity of the instrumentation, and the high manufacturing cost of the target product.

The method for preparing the hydrosilicate product by hydrothermal treatment of calcium carbonate with an alkaline silicic solution is the closest to the proposed method in its technical nature and the achieved result [2]

A drawback of the prior-art method is the target product's low modulus because of the impossibility of obtaining a product with the composition $\text{Na}_2\text{O} \cdot \text{CaO} \cdot 6\text{SiO}_2$ by the known method

The object of the invention is to increase the silicon modulus of the target product and to intensify the process.

The object is achieved by using an alkaline silicic solution, having a ratio of SiO_2 to $\text{Na}_2\text{O}_{\text{caust}}$ of 3.0–3.2 and a molar ratio of SiO_2 to CaCO_3 of 5.9–6.0, according to the method for preparing the silicate-calcium product by hydrothermal treatment of calcium carbonate with an alkaline silicic solution, and by running the process at 180–220°C

Increasing the temperature intensifies and assures the start of the process of the calcium carbonate decomposition. The formed CO_3^{2-} ion is absorbed with the sodium caustic remaining in the solution. Increasing the temperature from 180 to 220°C achieves the object as follows: the lower limit (180°C) increases and intensifies the degree of carbonization of an alkaline silicic solution already partially carbonized to 100–105%, decreases the silica content in the filtrate, and starts the complete precipitation of amorphous silica; the upper limit (220°C) results in the complete precipitation of silica. Thus, running the process at the indicated temperatures simplifies and intensifies the complete precipitation of silica. Further regulation of the process to obtain the target product is carried out with the CO_3^{2-} ion, which forms from calcium carbonate and totally precipitates silica from the solution. For this reason, the proposed values for the silicon modulus of the alkaline silicic solution $\text{SiO}_2/\text{Na}_2\text{O}_{\text{caust}} = 3.0\text{--}3.2$ with a soda content $(\text{SiO}_2) / (\text{Na}_2\text{O}_{\text{caust}} + \text{Na}_2\text{O}_{\text{carb}}) = 1.0\text{--}1.5$, and accordingly with a molar ratio $\text{SiO}_2/\text{CaCO}_3 = 5.9\text{--}6.0$ are used to achieve the object, because the process of the complete precipitation of amorphous silica by reaction with CaO is simplified and intensified. It is not advisable to exceed the limits of the proposed values for the silicon modulus, because a high-silicon product can be obtained with the composition of $\text{Na}_2\text{O} \cdot \text{CaO} \cdot 6\text{SiO}_2$ only within the indicated intervals.

The method is described as follows:

During the hydrochemical treatment of high-silica-containing rock, such as perlite, tripolite, quartz sand, diatomite, quartzite, etc., it is not necessary to prepare sodium and calcium metasilicate from the alkaline silicic solution. It is necessary to obtain immediately the alkaline silicic solution with a silicon modulus $\text{SiO}_2/\text{Na}_2\text{O}_{\text{caust}} = 3\text{--}3.2$ or $\text{SiO}_2/\text{Na}_2\text{O}_{\text{tot}} = 1.50\text{--}1.0$. After addition of CaCO_3 with a molecular ratio $\text{SiO}_2/\text{CaCO}_3 = 5.9\text{--}6$ or $\text{Na}_2\text{O} \cdot 3\text{SiO}_2/\text{CaCO}_3 = 3$ and partial carbonization to 85–95%, where $\text{Na}_2\text{O}_{\text{caust}}/\text{CaCO}_3 = 1.9\text{--}2$, the mixture is transferred to a continuously running autoclave for hydrothermal treatment at 180–220°C for 1–1.5 h, the obtained slurry is filtered. A sodium-calcium silicate with the composition $\text{Na}_2\text{O} \cdot \text{CaO} \cdot 6\text{SiO}_2$ is obtained in the precipitate.

The concentration of the alkaline silicic solution SiO_2 of 85–95 g/L, $\text{Na}_2\text{O}_{\text{caust}}$ of 30–33 g/L, and $\text{Na}_2\text{O}_{\text{carb}}$ of 30–62 g/L of carbonate alkali at the same time makes it possible to

accelerate the breakdown of the rocks; the obtained filtrate-soda solution, containing 4-5 g/L of SiO_2 , is transferred for the partial caustification and reuse, and the precipitated calcium carbonate is used for the preparation of sodium-calcium silicate.

During the autoclave process, CO_3^{2-} is removed from calcium carbonate, the already carbonized alkaline silicic solution is partially carbonized; the formed amorphous silica interacts with CaO, and conditions for the preparation of $\text{Na}_2\text{O}-\text{CaO}-6\text{SiO}_2$ are created. The degree of carbonization of the solution approaches 100-105%.

Example 1. 330 mL of the alkaline silica solution, with a concentration of SiO_2 of 90 g/L, $\text{Na}_2\text{O}_{\text{caust}}$ of 31 g/L, and $\text{Na}_2\text{O}_{\text{carb}}$ of 31.3 g/L with a silicon modulus of $\text{SiO}_2/\text{Na}_2\text{O}_{\text{caust}} = 3$ and molecular ratio of $\text{SiO}_2/\text{CaCO}_3 = 5.9-6$, is combined with 8.1 g of calcium carbonate and partially carbonized from 66 to 85.8%; the liquid phase in terms of alkali has the composition: $\text{Na}_2\text{O}_{\text{caust}}$ of 15.1 g/L and $\text{Na}_2\text{O}_{\text{carb}}$ of 48.23 g/L. The slurry is placed in the autoclave, the temperature is raised to 200°C, and the process is continued for 1.5 h. The obtained slurry is filtered and washed. The filtrate has the following composition: $\text{Na}_2\text{O}_{\text{carb}}$ of 43.7 g/L, $\text{Na}_2\text{O}_{\text{caust}}$ of 3.53 g/L, and SiO_2 of 4.15 g/L.

Chemical composition of the precipitate, %: SiO_2 , 69.19; CaO, 10.76; Na_2O , 11.29; calcination loss, 5.69; and moisture content 2.44. The precipitate has a moisture content of 58.7%. The precipitate is dried and as a result, a sodium-calcium silicate $\text{Na}_2\text{O}-\text{CaO}-6\text{SiO}_2$ is obtained, which is used as a raw material for glass, and the filtrate is returned for repeated caustification.

Example 2. 330 mL of the alkaline silicic solution, with a concentration of SiO_2 of 95 g/L, $\text{Na}_2\text{O}_{\text{caust}}$ of 31.76 g/L, and $\text{Na}_2\text{O}_{\text{carb}}$ of 61.35 g/L with a silicon modulus $\text{SiO}_2/\text{Na}_2\text{O}_{\text{caust}} = 3.15$ and molecular ratio of $\text{SiO}_2/\text{CaCO}_3 = 5.9-6$, is combined with 8.5 g of calcium carbonate and partially carbonized to 84.9%; the liquid phase in terms of alkali has the composition: $\text{Na}_2\text{O}_{\text{caust}}$ of 14.8 g/L and $\text{Na}_2\text{O}_{\text{carb}}$ of 79.03 g/L. The slurry is placed in an autoclave, the temperature is raised to 220°C, and the process is continued for 1.0 h. The obtained slurry is filtered and washed. The filtrate has the following composition: $\text{Na}_2\text{O}_{\text{carb}}$ of 75.23 g/L, $\text{Na}_2\text{O}_{\text{caust}}$ of 2.88 g/L, and SiO_2 of 4.26 g/L.

The chemical composition of the precipitate: %: SiO_2 , 69.93; CaO, 10.87; Na_2O , 12.84; calcination loss 4.97; and moisture content, 2.17. The precipitate is dried and as a result, a sodium-calcium silicate $\text{Na}_2\text{O}-\text{CaO}-6\text{SiO}_2$ is obtained, which serves as a raw material for glass and the filtrate is returned to the cycle for repeated caustification.

Example 3. 330 mL of the alkaline silicic solution, with a concentration of SiO_2 of 86.4 g/L, $\text{Na}_2\text{O}_{\text{caust}}$ of 27.6 g/L, $\text{Na}_2\text{O}_{\text{carb}}$ of 60.85 g/L, with a silicon modulus of $\text{SiO}_2/\text{Na}_2\text{O}_{\text{caust}} = 3.12$

and molecular ratio $\text{SiO}_2/\text{CaCO}_3 = 5.9-6$, is combined with 7.5 g of calcium carbonate and partially carbonized to 84.5%; the liquid phase in terms of alkali has the following composition: $\text{Na}_2\text{O}_{\text{caust}}$ of 12.26 g/L and $\text{Na}_2\text{O}_{\text{carb}}$ of 76.72 g/L. The slurry is placed in an autoclave, the temperature is raised to 180°C , and the process is continued for 1.5 h. The obtained slurry is filtered and washed. The filtrate has the following composition: $\text{Na}_2\text{O}_{\text{carb}}$, 74.86 g/L; $\text{Na}_2\text{O}_{\text{caust}}$, 3.12 g/L; and SiO_2 , 4.73 g/L.

Chemical composition, %: SiO_2 , 68.75; CaO , 10.32; Na_2O , 11.89; calcination loss, 6.01; moisture content, 2.94. The precipitate is dried and as a result, a sodium-calcium silicate $\text{Na}_2\text{O}-\text{CaO}-6\text{SiO}_2$ is obtained, which is used as a raw material for glass, and the filtrate is returned to the cycle for repeated caustification.

Claim

Method for preparing a silicate-calcium product by hydrothermal treatment of calcium carbonate with an alkaline silicic solution, characterized in that to intensify the process and to increase the silicon modulus of the target product, an alkaline silicic solution is used at a ratio of SiO_2 to $\text{Na}_2\text{O}_{\text{caust}}$ of 3.0-3.2, and a molar ratio of SiO_2 to CaCO_3 of 5.9-6.0, and the process is run at a temperature of $180-220^\circ\text{C}$.

References considered in the examination

- 1 USSR Certificate of Authorship No. 147585, class C 01 B 33/24, 1961.
- 2 USSR Certificate of Authorship with respect to application No. 2931498/23-26, class C 01 B 33/24, 1980.